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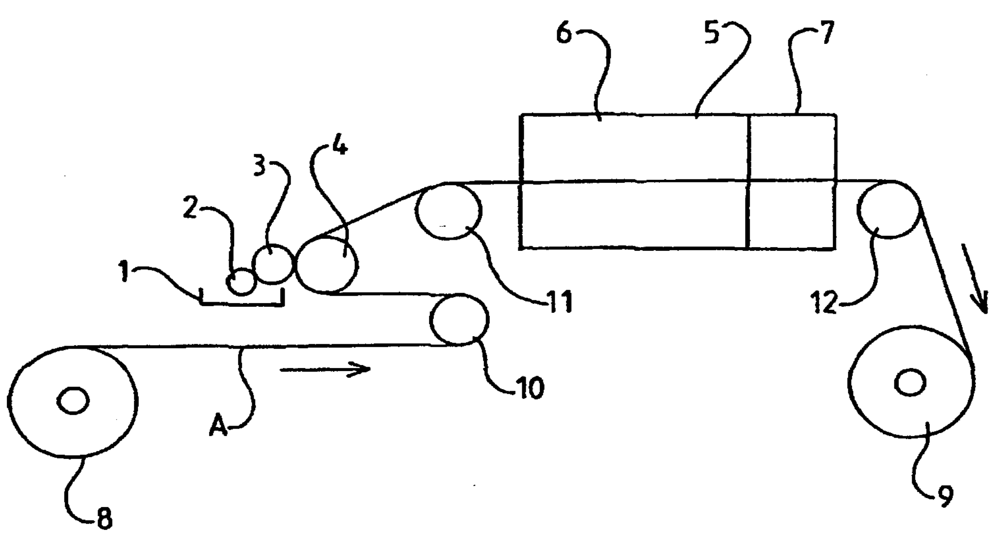
(54) Title: ALUMINIUM PRODUCT WITH EXCELLENT BRAZING CHARACTERISTICS



(57) Abstract: An aluminium product having excellent brazing characteristics having at least one flat surface coated with a brazing flux composition comprising brazing flux and a synthetic resin based, as its main constituent, on methacrylate homopolymer or a methacrylate copolymer, wherein the brazing flux is a reactive flux and in that the coating of brazing flux composition is free from metal and/or silicon particles.

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Aluminium product with excellent brazing characteristics

The invention relates to an aluminium product having excellent brazing characteristics having at least one flat surface coated with a brazing flux composition comprising brazing flux and a synthetic resin based, as its main constituent, as methacrylate homopolymer or a methacrylate copolymer.

Such an aluminium product is known from GB-A-2.334.531.

In this known product the coating contains braze particles, especially metallic particles or Si-particles or mixtures thereof, in order to obtained the required brazing connection.

The use of such braze particles has a number of disadvantages.

In the first place the braze particles must be mixed with the binder of the coating, which is in fact a physical mixture and therefore subject to separation and loss of homogenity in the coating.

In general the size of the braze particle tends to be large in relationship to the coating thickness so that particles stand proud of the coated surface thereby causing a roughened surface which will inhibit sliding of tubes during handling. Moreover mechanical abrasion can take place between contacting surfaces of two products during handling, transport machining etc., thereby changing or even destroying the brazing characteristics of the applied coating.

The use of braze particles and especially of Si-particles can give localised surface reactions which lead to irregular thinking of the surface of the product during brazing, or the generation of brazing faults such as burn through.

It is therefor an object of the invention to provide an aluminium product as described above in which the above mentioned problems are avoided.

This obtained in that the brazing flux is a reactive flux and in that the coating of brazing flux is free from metal and / or silicon particles.

A reactive flux is a flux which contains a chemical composition which as result of the reaction between aluminium and the chemical composition at elevated temperature results in in situ formation of a brazing alloy which can be brazed at that temperature.

Preferably the reactive flux is a fluorosilicate or potassiumfluorozincate of potassium but cæsium or rubidium salts are also effective.

Such reactive flux systems have been described in more detail in WO-A-98.10887 and the content of this disclosure is herewith incorporated by reference.

The weight ratio of the brazing flux to the synthetic resin in the flux composition is in the range from 9:1 to 3:2. When the weight ratio of the reactive flux exceeds 9, adhesion of the composition to the aluminium material becomes insufficient and the coating tends to cause flaking, whereas at less than 3:2 the excessive proportion synthetic resin can harm the brazing atmosphere which alter braze characteristics and raise the cost.

The invention also relates to a method for manufacturing an aluminium product having excellent brazing characteristics having at least one flat surface which is coated with a mixed flux composition comprising a brazing flux and as organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved.

This method is characterized in that the brazing flux is a reactive flux, in that the coating of brazing flux is free from metal and / or silicon particles and in that the coating is applied by means of a reverse roll coating technique, whereupon the applied coating is heated and dried to evaporate the organic solvent in the mixed flux composition. Roll-transfer printing can also be used as an application method but reverse roll coating is preferred since it offers superior control of the quality of the deposited layer.

As for the synthetic resins to be used in the present invention, those mainly comprising a homopolymer of a methacrylate or a copolymer of two or more methacrylates are preferred. Given as specific examples of such a methacrylic acid ester are methyl methacrylate, ethyl methacrylate, propyl methacrylate, 2-methylpromyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-etylhexyl methacrylate, octyl methacrylate-isodecyl methacrylate, lauryl methacrylate, tridecyl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, diathylaminoethyl methacrylate, 2-hydroxyethyl methacrylate,

dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, glycidyl methacrylate, metaterahydrofurfuryl methacrylate, and the like.

Reverse roll coat or roll-transfer printing equipment, for example has a configuration illustrated in Figure 1, wherein an aluminium-extruded multi-cavity flat tube A supplied from a rewinding unit 8 is sent to a composition application step via a feeder roll 10. In the application step, the composition stored in a composition container 1 is picked up by an attached pick-up roll 2, transferred to an application roll 3, and then applied to the surface of the aluminium-extruded multi-cavity flat tube A that passes through the application roll 3 and a back-up roll 4.

The aluminium-extruded multi-cavity flat tube A coated with a composition is sent through a feeder roll 11 to an oven 5 such as a convection oven that consists of a drying zone 6 and a cooling zone 7. The aluminium-extruded multi-cavity flat tube A, after being heated in the drying zone 6 to a temperature of about 200° to 300°C, is cooled and wound up by a winder unit 9, after passing through a feeder roll 12. While a convection heating system is suitable as the heating system for the furnace, radiant heating with far-infrared rays could also be used, in conjuction with a supply of air to promote evaporation of organic solvents.

The aluminium-extruded multi-cavity flat tube A passes through the furnace 5 usually within several seconds during which time the organic convents contained in the composition coated on it evaporate, leaving a coating comprising flux and synthetic resin, on one of the flat surfaces of the aluminium-extruded multi-cavity flat tube. While Figure 1 illustrates the equipment configuration for applying a composition on just one side of the flat surface of the aluminium-extruded multi-cavity flat tube, both sides of the flat tube can be coated by adding one more composition container and roll set.

The present invention will be explained in more detail referring to the following examples.

Examples

The binder system was based upon Paraloid B 48 (Rohm & Haas). A flux to binder ratio of 3:2 was found satisfactorily from a brazing aspect and a coating was produced. A batch of K_2SiF_6 was used in the trials. This material was synthesised and screened to ensure that maximum particle size would be less than the dry coating thickness of the coating on the tube. (i.e. <30 μm) The Paraloid B 48 was available in a 40% solids solution in Xylene solvent.

The bar coat trials to adjust coating parameters are summarised below:

Flux (gram)	B 48 solution (ml)	Xylene (ml)	Bar coater	Coating dry film thickness	g/m^2 flux
75	125	-	brown	>50	>70
75	125	20	blue	45	>50
75	125	40	grey (036)	30	40
75	125	60	grey (036)	25	± 30

<u>Evaluation coating</u>

MPE tube samples were coated using the 036 bar coater. Drying / cure of the wet coating utilised the standard oven setting, i.e. 1 1/2 minutes in oven set at 240°C. The dry film thickness was confirmed as 25 to 28 μm when checked using an eddy current coating thickness measuring device. Reverse impact tests using 60, 40 and 20 lb.in. showed no loss of adhesion on the indentation and no loss of coating when tested with adhesive tape (Sellotape). Coated tube samples were subjected to a flat bend and again the adhesion was tested by means of adhesive tape. Only a slight discolouring of the tape was observed. The surface of the dry coating was relatively smooth and did not show any tendency to stick to adjacent coated surfaces. Tubes coated in the manner described above were assembled with unclad fins and brazed successfully in a CAB braze oven.

<u>Coating</u>

Sufficient coating material was made up to fill the tray of a laboratory roll coat equipment. In all, about 2 litres of coating was made up according to the 3:2 flux to Paraloid B 48 ratio. The solvent used for the B 48 was DBE (dibasic ester). The coater was set up in 2 roll conformation. (i.e. one pick-up roll and one applicator roll). The coating was applied to the flat tube surface in reverse roll coating mode. The applicator roll was adjusted to give the desired dry film thickness of coating (25 to 28 μm) and a batch of tubes was coated and the wet coating dried. Thereafter, the tubes were coated on their reverse side and the wet film dried once more so that each flat face of the tube received an equivalent coating thickness. In order to establish the minimum requirements for drying the coating some tubes were placed in the laboratory drying oven for only 45 seconds, half the normal dwell time. Testing of the coating by means of reverse impact and bend testing showed that the coating was in no way inferior to the tube which had received the long cure time.

Assessment of coated tube

A coated tube sample was weighed and then placed in a laboratory muffle furnace at 350°C for 10 minutes. The tube was then carefully removed so as not to disturb the remaining coating and, when cool, was reweighed. The remaining coating was then physically removed by wiping with paper tissue and the tube was then reweighed. From the weight differences the coating thickness could be defined and hence the amount of flux.

CAB brazing of roll coated tubes

5 sample cores were built using coated MPE tube and unclad fin material. The samples were passed through the CAB oven using the following conditions and settings:

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Belt speed (in/min)
1	400	450	585	605	610	614	614	12
2	400	450	585	605	610	614	614	15
3	450	480	500	550	580	600	600	9
4	450	480	500	580	600	610	580	12
5	450	480	500	580	600	610	610	15

Key features of the braze operation are summarised in the table below:

	Peak temp. °C	Time >577°C (min)	Time >595°C (mini)	Time >600°C (min)	Ramp rate (°C/min) 400 to 577°C	Colour	Braze fillet
1	613	445	345	300	37	V. dark on outer tube surface	Basically OK fillets
2	608	3	2	2,6	68	Lighter than #1	OK where good contact
3	600	4,5	2,1	-	30	Brown tint even on uncoated faces	Poor
4	604	3,7	2,15	1,35	68	Similar to #2	Similar to #2
5	605	2,4	1,6	1,4	61	Darker than #2 Dark within core	Braze fillets small

The resulting braze joints showed excellent fillet formation and no free Si-particles were present in the brazed joints.

Claims

1. An aluminium product having excellent brazing characteristics having at least one flat surface coated with a brazing flux composition comprising brazing flux and a synthetic resin based, as its main constituent, on methacrylate homopolymer or a methacrylate copolymer, characterized in that the brazing flux is a reactive flux and in that the coating of brazing flux composition is free from metal and / or silicon particles.

2. An aluminium product according to claim 1, characterized in that the reactive flux contains potassiumfluorosilicate and / or potassiumfluorozincate.

3. An aluminium product according to claim 1 or 2, characterized in that the weight ratio of the brazing flux to the synthetic resin in the flux composition is in the range from 9:1 to 3:2.

4. The aluminium product of claim 2, characterized in that the brazing flux is composed of 0 - 100% by weight of K_2SiF_6, 0 - 100% by weight of $KZnF_3$ and / or 0 - 50% by weight of potassium fluoroaluminate.

5. The aluminium product according to claim 4, characterized in that the potassium fluoroaluminate is $KAlF_4$ and / or K_2AlF_5.

6. The aluminium product according to claim 4 that the brazing flux contains 6 - 100% by weight of K_2SiF_6.

7. An aluminium product according to claim 2, characterized in that the brazing flux contains 70 - 90% by weight K_2SiF_6 and 30 - 10% by weight of $KAlF_4$.

8. An aluminium product according to any one fo the claims 2, 4, 5, 6 or 7, characterized in that the at least part of the potassium salts is substituted by corresponding salts of Caesium and / or Rb.

9. An aluminium product according to any one of the preceeding claims, characterized in that the amount of reactive flux is selected in such a way that the amount of free Si, Zn or Zn + Si on the coated surface is within the range 1 to 7 g/m^2.

10. An aluminium product according to any one of the preceeding claims, c h a r a c t e r i z e d i n t h a t the synthetic resin comprises at least 10% by weight of a resin commercially available as Paraloid B 48 of Rohm & Haas.

11.A method for manufacturing an aluminium product having excellent brazing characteristics having at least one flat surface which is coated with a mixed flux composition comprising a brazing flux and an organic solvent in which a synthetic resin base, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer, c h a r a c t e r i z e d i n t h a t the brazing flux is a reactive flux, in that the coating of brazing flux is free from metal and / or silicon particles and in hat the coating is applied by means of a roll-transfer coating technique, whereupon the applied coating is heated and dried to evaporate the organic solvent in the mixed flux composition.

12. The method according to claim 10, c h a r a c t e r i z e d i n t h a t the atomic ratio of carbon to oxygen in the molecular structure of said organic solvent is a value between 2 and 3.

13. The method according to claims 10 or 11, c h a r a c t e r i z e d i n t h a t the viscosity of the mixed flux composition is between 100 and 10 000 mPA-s.

14. The method according to claims 10, 11 or 12, c h a r a c t e r i z e d i n t h a t the weight ratio of the flux powders to the synthetic resin comprised within the mixed flux composition is in the range from 9:1 to 3:2.

15. The method according to any one of the claims 11-14, c h a r a c t e r i z e d i n t h a t the synthetic resin comprises at least 10% by weight of a resin commercially available as Paraloid B 48 of Rohm & Haas.

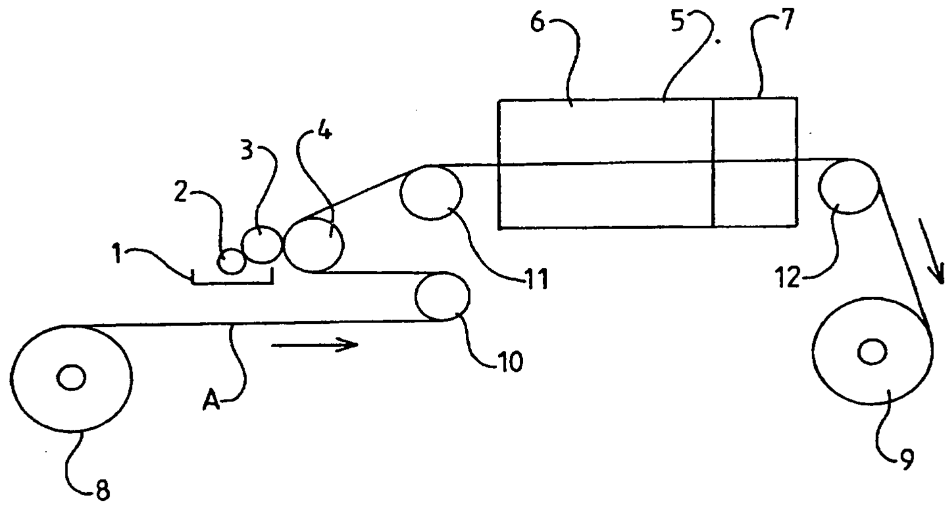

Fig. 1

INTERNATIONAL SEARCH REPORT

Inter   onal Application No
PCT/EP 99/09162

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B23K35/36 B23K35/363

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 13 111 A (SOLVAY FLUOR & DERIVATE) 30 September 1999 (1999-09-30) page 3, line 19 - line 41 ---	1,2,11
Y	DE 196 36 897 A (SOLVAY FLUOR & DERIVATE) 12 March 1998 (1998-03-12) cited in the application the whole document ---	1-15
Y	GB 2 334 531 A (DENSO CORP ;SUMITOMO LIGHT METAL IND (JP)) 25 August 1999 (1999-08-25) cited in the application claims; examples ---	1-15
A	DE 43 39 498 A (CASTOLIN SA) 24 May 1995 (1995-05-24) --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 July 2000	28/07/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Inter   onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 193 676 A (CASTOLIN) 22 February 1974 (1974-02-22) ---	
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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